IPST Technical Paper Series Number 591

Measurement of Delignification Diversity Within Kraft Pulping Processes

B. Boyer and A. Rudie

August 1995

Submitted to
TAPPI Pulping Conference
October 1–5, 1995
Chicago, Illinois

MEASUREMENT OF DELIGNIFICATION DIVERSITY WITHIN KRAFT PULPING PROCESSES

Brian Boyer
Graduate Student
IPST
Atlanta, GA 30318

Alan Rudie
Associate Professor
IPST
Atlanta, GA 30318

ABSTRACT

Measurements of the variation in kraft pulp lignin content have been the subject of intense interest for several years. Historically, macroscale variation has been determined in mill studies using hanging-baskets within batch digesters; at which time, lignin content variability was observed and related to chip location and thickness. On a smaller scale, slices of cooked chips have been examined to determine lignin content variability. Unfortunately, few data are available on lignin content variability within and between individual fibers. Available data do suggest, however, that a high level of interfiber delignification diversity should be present. This study has measured lignin content variability between individual kraft softwood pulp fibers using two laboratory methods: density gradient column distributions and single-fiber FTIR microspectroscopy. Large variations in fiber-to-fiber lignin content were observed in a 17.6 kappa number pulp, a 78.0 kappa number pulp, and a 21.8 kappa number mill-produced pulp.

Traditionally, bleachable grade softwood pulp has been delignified to a kappa number of approximately 30 to optimize strength, yield, and production capacity. Today, the trend is to pulp toward lower kappa numbers, with the goal of minimizing bleach plant effluent. However, losses in pulp production, yield, and quality can occur. A measure of the variation in single-fiber lignin content may lead to a better understanding of this problem, thus minimizing losses.

Nonuniform pulp is a result of variations within and between digesters (1,2). Variations between digesters can result from fluctuations in chemical charge, H-factor calculation, furnish swings, etc. Within digester variation may result from oversized chips, inhomogeneous or insufficient liquor flux, and unequal temperature and/or chemical distribution inside and outside of the chips (2-5). Improvements in uniformity generally imply that there are less overcooked and undercooked chips (1).

Uniform delignification results in pulps of higher strength and yield, along with reductions in bleaching chemical demand (1,3,6,7). The current work demonstrates lignin content variations in a 17.6 kappa number pulp and 78.0 kappa number pulp, and a 21.8 kappa number mill produced pulp. All pulp samples are softwood kraft. In addition, an acid chlorite holopulp sample will be used to determine the inherent density variation in a lignin-free pulp.

Unbleached laboratory pulps are often considered the realistic quality potential of a given fiber source (4,8,9). Results from quality comparisons of mill pulps to laboratory or pilot-plant pulps are readily available in the literature (1,3,4,8,9,10-13,14,15).

BATCH DIGESTER STUDIES

Blume (10) studied process variations as early as the 1950s, using a "hanging-basket" within batch digesters. Subsequently, MacLeod etal., (4,9,14) have measured pulp quality in batch digesters using similar forms of this technique. It was discovered that pulp inside a batch digester is capable of having strength values near those of laboratory pulps. After blowing, pulp strength can be 20-30% lower (14). Similarly, Tikka etal. (1,16), Anderson and Rea (11), and Gullichsen etal. (3) each used three-basket arrays to measure variations in pulp strength and lignin content within batch digesters.

CONTINUOUS DIGESTER STUDIES

The only studies published on within digester pulp variation were performed over 30 years ago by Knutsson and Stockman (12) and Annergren, Ohrn, and Rydholm (13). This work used a through-the-wall sampling technique developed by Jansson (17) of Kamyr AB. Similar to the later findings of MacLeod (14), the discovery was that high-quality pulp was present prior to discharge from the digester.

Interestingly, lignin content variation has been observed using on-line kappa number analyzers (18,19). A constant fluctuation of at least ± 5-10% has been observed (19), but did not coincide with standard kappa number profiles. This suggests that the mixed stock may be masking a significant lignin content variation existing between fibers (4).

A key element in the analysis of the lignin content variation between fibers will make use of the density gradient column concept (20,21).

THE DENSITY GRADIENT COLUMN

Essentially, the density gradient column is a mixture of completely miscible solvents whose composition and density varies with column height. Density gradient columns are very

sensitive methods to measure density distributions, and have the ability to differentiate density differences down to about 10^{-7}g/ml (20). This resolution is more than sufficient because most densities are reported only to the fifth decimal place.

Development in the Pulp and Paper Industry

Lignin content uniformity was first qualitatively measured by Paulson (22). Wandelt and Mroz (23) have used a similar pulp density method to estimate yield from NSSC pulps.

All density separation techniques for wood assume that the individual densities of wood fiber components are additive, where lignin, holocellulose, and α-cellulose have specific gravities of 1.335, 1.521, and 1.528, respectively (24). Therefore, the density of an unbleached fiber is assumed to be inversely related to its content of non-cellulosic material, especially lignin.

Paulson (22) looked at fiber density distributions within a density gradient column, and fractionated fibers by dispersing them in columns of uniform density. The conclusion was that chip thickness and reaction wood are contributors to nonuniformity.

Tichy and Procter (6) used this method to quantitatively measure variations in lignin content and relate them to pulp quality. Although lignin content uniformity was found to be wood species dependent, a relationship seemed to exist for the lignin content variation between fibers and pulp quality.

Horng, Mackie, and Tichy (8) have shown that a definite relationship exists between pulp strength, liquor flux, and interfiber uniformity in continuous digesters using the density gradient column.

HISTORY OF INFRARED LIGNIN ANALYSIS

FTIR Lignocellulose Determination

Several infrared techniques have been used extensively to quantify wood and its components (25-31). A common problem is that infrared peaks can be broad and overlapping in complex spectra of this type.

Subtraction techniques can be used to simplify a complex spectrum by subtracting a reference spectrum until there is a growth of negative peaks in the original spectrum (25). Although this method may be fine for qualitative work, quantitative analyses should use a less subjective subtraction technique to ensure reproducibility.

Mathematical algorithms based on component ratios or numerical methods have been used objectively to acquire reproducible information from multicomponent spectra. Component ratios make the assumption that component spectra are orthogonal, where the overall matrix does not have an effect on individual absorbencies. Numerical methods, such as least-square-fits or regression analyses, determine the most significant correlations between the sample set and calibration set to determine which absorbencies to select for quantitative comparisons. As the number of statistically significant absorbencies increases, the accuracy of the system also increases. However, the numerical fitting methods assume that the contribution of each component spectra is linear. It is also assumed that all spectral component contributions are known.

Schultz and Burns (26) used four peaks to determine lignin, hemicellulose, and cellulose composition with FTIR by secondary analysis combined with stepwise regression. Standard KBr pellet techniques were combined with first-derivative spectra to avoid difficulties in baseline shift and accentuate small spectral differences. Since first derivative spectra give negative peaks, the absolute value of the first-derivative was used in the 1600-900 cm^{-1} spectral region. The R^2 values for softwood were 0.98, 0.83 for lignin and cellulose, respectively. The fit for hemicellulose was too poor for consideration. The R^2 values for hardwood were 0.97, 0.91, and 0.90 for lignin, cellulose, and hemicellulose, respectively.

Backa and Brolin (27) used DRIFT (diffuse reflectance infrared fourier transform) in combination with partial least squares analysis. A total of 232 peaks were selected outside the range of 2800 and 1750 cm^{-1}, and between 3300 and 450 cm^{-1}. A few peaks were chosen according to Faix (28) and Schultz etal. (29), and all were approximately 10 cm^{-1} apart. The standard error provided by this technique was ±2.75% for lignin content determination. Wallbacks etal. (30) used a similar procedure and obtained a standard error of ±3.3% for lignin determination.

The advantage of the partial least squares technique is that the number of samples may be less than the number of spectral bands used in the determination. In addition, the technique does not require spectral orthogonality; all inherent spectral information may be used for quantification.

More recently, Friese and Banerjee (31) developed a unique computational method to determine pulp lignin content. DRIFT spectra were obtained using disks that were cut from air-dried pulps and stacked in a sample cup. The premise of this procedure was that spectral complexity decreases as constituent spectra are subtracted. One measure of complexity is the integrated positive and negative area of first-derivative spectra. Therefore, if a fraction of a component spectrum is subtracted stepwise from the multi-component spectrum, and the area of the first-derivative

spectra is obtained, the component spectrum will be factored out when the first-derivative area minimizes. The lignin:cellulose ratio can be used to determine lignin content relative to cellulose content. This ratio is then linearly regressed to calibration data obtained by standard wet-lab techniques, where an excellent relationship exists. The uncertainty of the technique is on the order of ±2 kappa units in the 10-40 kappa number range.

EXPERIMENTAL METHODS

Pulping of southern yellow pine was performed in an M/K digester using 3mm x 15mm x 25mm rotary cut veneer chips. A constant cooking temperature of 165°C, EA of 40gpl, liquor:wood ratio of 6:1, and a sulfidity of 30% (based on AA) produced the pulps used in this study. Kappa numbers of 17.6 and 78.0 were produced using H-factors of 2000 and 400, respectively. Presteaming and vacuum impregnation were employed.

The density gradient column is formed from a mixture of chloroform and tetrachloroethylene. A 2mg O.D. pulp sample is freeze-dried and vacuum impregnated in 80ml of chloroform, well dispersed, and transferred to the bottom of the density gradient column. Formation of gradient occurs underneath the sample while floating the fibers and chloroform.

Imaging and data acquisition from the column is achieved through the use of polarized back-lighting and high contrast black-and-white photography through cross-polarized light. Image analysis software has been used to determine relative fiber density distributions.

Infrared analysis was performed using a Nicolet Nic-Plan instrument with a microscope attachment. Single fibers were analyzed using a KBr reference in the transmission mode.

RESULTS

Density Gradient Column Analyses

Density gradient column work has shown the variations in lignin content between fibers. Figure 1 is descriptive of a uniform thin chip pulp of kappa number 17.6, whereas Fig. 2 is descriptive of a uniform thin chip pulp of kappa number 78.0. The distributions suggest that the higher kappa number pulp, although produced from thin chips, varies more in lignin content than the lower kappa number thin chip pulp.

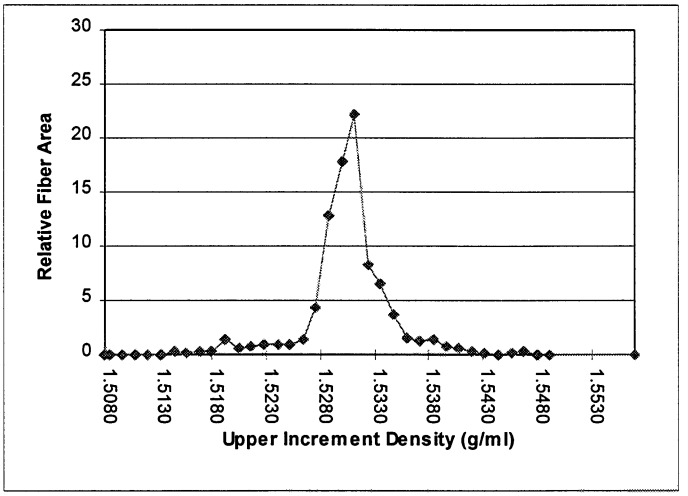

Figure 1. Lignin variability in 17.6 kappa number pulp.

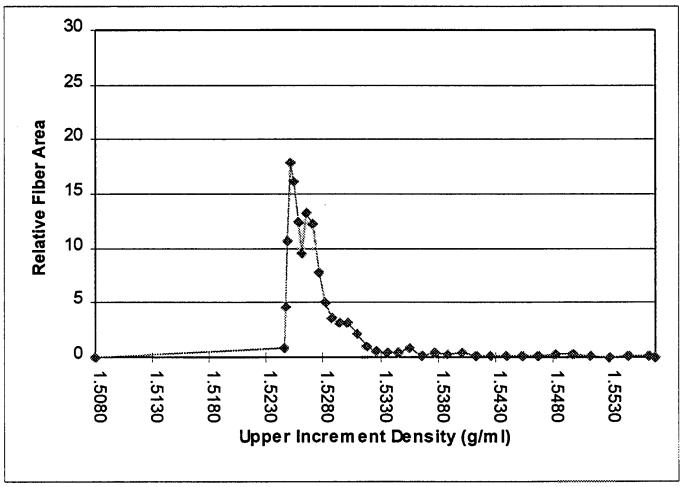

Figure 2. Lignin variability in 78.0 kappa number pulp.

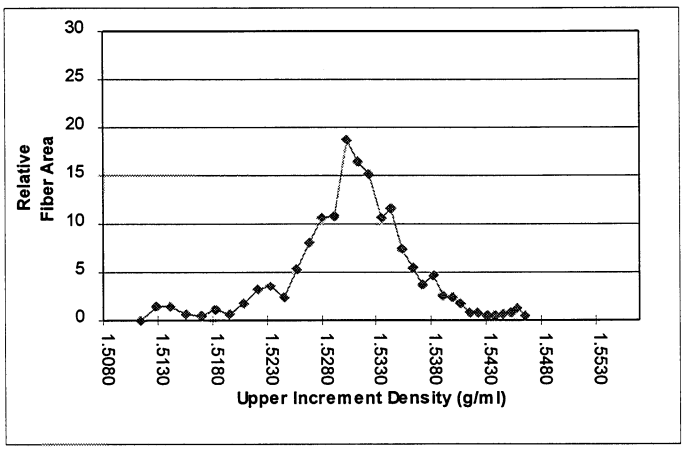

Figure 3. Lignin variability in a mill-produced 21.8 kappa number pulp.

Interestingly, Fig. 3. is representative of a typical mill-produced low kappa number softwood pulp. Lignin content variability is more pronounced in this distribution than in the laboratory pulp distributions.

Analyses of fiber density distributions will need to include an estimate of the inherent density variability that exists between lignin-free fibers. Acid-chlorite holopulp fibers were obtained from the 17.6 kappa number pulp and dispersed in the density gradient column, as shown in Fig.4.

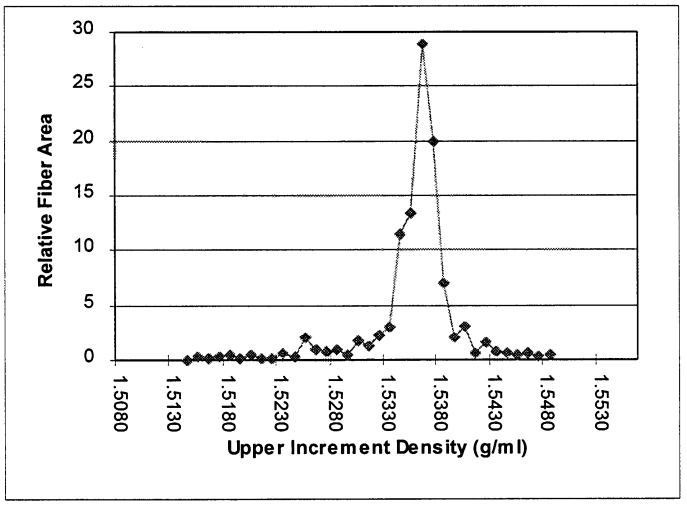

Figure 4. Density variation in acid-chlorite holopulp.

Table 1 lists the descriptive statistics of the four fiber density distributions.

Table 1. Descriptive Statistics of Pulp Lignin Variation.

Pulp Sample	78.0 kappa Lab Pulp	17.6 kappa Lab Pulp	21.8 kappa Mill Pulp	Holopulp
Mean Density (g/ml)	1.5270	1.5306	1.5313	1.5360
Standard Deviation	0.0050	0.0049	0.0070	0.0053
Mode Density (g/ml)	1.5252	1.5312	1.5303	1.5367
Skewness	-3.7503	0.2970	0.3274	1.1751
Kurtosis	19.4859	1.5309	-0.1095	2.3550

As can be seen, the holopulp distribution appears more uniform than the kraft pulps, however, the standard deviation in density does not reveal this apparent uniformity. An explanation for this may be that the distribution tail-sections are partially comprised of fibers clinging to the column walls and other column imaging artifacts. This difficulty will be addressed in future studies.

FTIR Spectral Analyses

Infrared KBr pellet spectra were calibrated to traditional wet-lab analyses of lignin content. Figure 5 shows the calibration curve and regression equation.

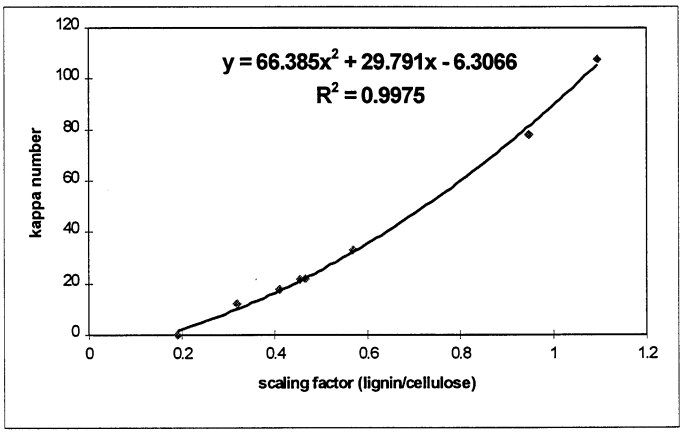

Figure 5. Calibration curve for FTIR spectral analyses.

Pulp samples of kappa numbers 108, 78.0, 32.9, 21.5, 17.6, 11.9, and a bleached fiber sample were regressed against the lignin/cellulose subtraction factor ratio. Dioxane lignin and cotton linters spectra are individually subtracted from the whole spectra, where the cotton linters subtraction factor is used as an internal standard in each case. The regression equation is then used to evaluate fiber lignin content variation.

Figure 6 is an example of a random sampling of sixteen individual fibers from the 78.0 kappa number pulp. The shape of the distribution is similar to that of the fiber area vs. density distribution.

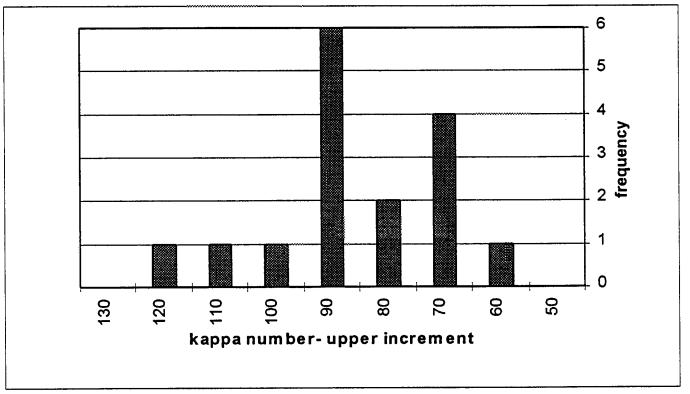

Figure 6. Fiber frequency vs. kappa number in 78.0 kappa number pulp.

Scaling factor values and ratios are given in Table 2 for the sixteen individual fibers analyzed from the 78.0 kappa number pulp. Interestingly, the mean spectral kappa number calculated from the quadratic fit is very close to the kappa number derived from wet-lab techniques.

Table 2. Spectral kappa number calculations

cellulose scaling factor	lignin scaling factor	scaling factor ratio (lig./cell.)	spectral kappa number
1.1197	1.008	0.900241	80.3
1.2818	1.0186	0.794664	70.1
1.2937	1.0231	0.790832	69.8
0.8467	0.99681	1.177288	106.9
0.74515	0.969159	1.300623	118.8
0.95587	0.79659	0.833366	73.8
0.90109	0.70438	0.781698	68.9
1.0661	0.76981	0.72208	63.1
1.0611	1.0474	0.987089	88.6
1.3067	0.86014	0.658254	57.0
0.96856	0.92878	0.958929	85.9
1.4477	1.1217	0.774815	68.2
1.3303	1.2092	0.908968	81.1
0.70586	0.63597	0.900986	80.3
1.0169	1.0242	1.007179	90.6
1.0962	1.0898	0.994162	89.3
Mean Kappa			**80.8**

SUMMARY

Density gradient column and FTIR microscopic analyses appear to provide meaningful data regarding individual fiber lignin content. Mill produced pulp has shown a much larger standard deviation in lignin content than laboratory produced kraft pulps. Concurrently, FTIR microscopic analyses of a random fiber sample has shown a frequency distribution similar to that of its respective density gradient column. Future work will address the implications of lignin content variation between and within fibers on pulp quality parameters.

ACKNOWLEDGEMENTS

I would to thank the Institute of Paper Science and Technology, the Board of Trustees, all member companies, and individual contributors. Special thanks go to research committee members Dr. Earl Malcolm and Dr. Thomas McDonough, and IPST alumnus Mike Friese for his assistance with FTIR spectral analyses.

LITERATURE CITED

1. Tikka, P.; and Kovasin, K., *Paperi ja Puu*, "Displacement vs. Conventional Batch Kraft Pulping: Delignification Patterns and Pulp Strength Delivery,". 72(8): 774 (1990).

2. Gustafson, R.R., Jimenez, G., McKean, W.T., and Chian, D., *Tappi Journal*, "The Role of Penetration and Diffusion in Nonuniform Pulping of Softwood Chips," (8): 163 (1989).

3. Gullichsen, J., Kolehmainen, H., and Sundqvist, H., *Paperi ja Puu*, "On the Nonuniformity of the Kraft Cook," 74(6): 486 (1992).

4. Tikka, P., MacLeod, J.M., and Kovasin, K., *Tappi Journal* "Chemical and Physical Performance of Kraft Cooking: The Impact of Process Alternatives," (1): 137 (1991).

5. Jimenez, G., McKean, W.T., and Gustafson, R.R., *Tappi Journal*, "Using a Kraft Pulping Model to Improve Pulp Uniformity," (7): 173 (1990).

6. Tichy, J., and Procter, A.R., *Svensk-Papperstidning,* Measurement and Significance of Lignin Content Uniformity in Unbleached Kraft Pulps," 84(15): R116 (1981).

7. Atkinson, E.S., and Partridge, H. De V., *Tappi Journal,* "Effects of Mixing and Degree of Chlorination on Quality and Bleaching Costs," 49(2): 66A (1966).

8. Horng, A.J., Mackie, D.M., and Tichy, J., *Tappi Journal,* "Factors Affecting Pulp Quality from Continuous Digesters," (12): 75 (1987).

9. MacLeod, J.M., *76th Annual Meeting, Technical Section. CPPA,* "Is Unbleached Softwood Kraft Pulp Strongest at 30 Kappa Number?:" A37 (1990).

10. Blume, W.M., *Tappi Journal,* "Basket cooking in Mill Digesters," 37(12): 145A (1954).

11. Anderson, D., and Rea, M., *Spring Conference. CPPA*, "Improving Pulp Uniformity with Triple Hanging Baskets:" (1990).

12. Knutsson, T., and Stockman, L., *Tappi Journal*, "The Effect of Mechanical Treatment during the Final Stages of the Cook on the Beating Properties and Strength of Sulphate Pulp," 41(11): 704 (1958).

13. Annergren, G.E., Ohrn, O.E., and Rydholm, S.A., *Svensk-Papperstidning,* "Kraft Pulp Quality from Batch and Continuous Cooking," 66(4): 110 (1963).

14. MacLeod, J.M., *Tappi Journal*, "Basket Cases: Kraft Pulp Strength Variability Within a Batch Digester," (10): 185 (1990).

15. Tikka, P., *Tappi Pulping Conference Proceedings,* "Conditions to Extend Kraft Cooking Successfully:" 699 (1992).

16. Tikka, P., Tahkanen, H., and Kovasin, K., *Tappi Pulping Conference Proceedings,* "Chip Thickness vs. Kraft Pulping Performance: Part I. Experiments by Multiple Hanging Baskets in Batch Digesters:" 555 (1992).

17. Jansson, L., Lagergren, S., and Rydholm, S., *Tappi Journal,* "Studies on the Interfiber Bonds of Wood: Part III. An Investigation on Hot Stock Pressure Refining of NSSC Pulp," 42(8): 649 (1959).

18. Kubulnieks, E., Lundqvist, S., and Pettersson, T., *Tappi Journal,* "The STFI OPTI-Kappi Analyzer: Applications and Accuracy," (11): 38 (1987).

19. Tikka, P., and Piiroinen, P., *Pulp and Paper Canada,* "Cooking Liquor Analyzer: A New Tool for Controlling a Continuous Digester," 88(10): T387 (1987).

20. Oster, G., and Yamamoto, M., *Chemical Reviews,* "Density Gradient Techniques," 63: 257 (1963).

21. Tessler, S., Woodberry, N.T., and Mark, H., *Journal of Polymer Science (Letters to the Editors)*, "Application of the Density-Gradient Tube in Fiber Research," 1(5): 437 (1946).

22. Paulson, J.C., *Svensk-Papperstidning,* "Unbleached Pulp Uniformity in Prehydrolysis-Kraft Pulp from Slash Pine," 74(13-14): 397 (1971).

23. Wandelt, P., and Mroz, W., *Tappi Journal,* "A Rapid Method for Measuring Yield in Semichemical Pulping Processes," (3): 203 (1992).

24. Stamm, A.J., and Sanders, H.T., *Tappi Journal,* "Specific Gravity of the Wood Substance of Loblolly Pine as Affected by Chemical Composition," 49(9): 397 (1966).

25. Griffith, P.R., and de Haseth, J.A., *Fourier Transform Infrared Spectrometry*, Vol 83. John Wiley and Sons, Publishers. Institute of Paper Science and Technology, Atlanta, GA (1986).

26. Schultz, T.P., and Burns, D.A., *Tappi Journal,* "Rapid Secondary Analysis of Lignocellulose: Comparison of NIR and FTIR," (5): 209 (1990).

27. Backa, S., and Brolin, A., *Tappi Journal,* "Determination of Pulp Characteristics by Diffuse Reflectance FTIR," (5): 218 (1991).

28. Faix, O., *Holzforschung*, "Investigation of Lignin Polymer Models by FTIR Spectroscopy," 40(5): 273 (1986).

29. Schultz, T.P. etal., *Analytical Chemistry*, "Rapid Determination of Lignocellulosics by Diffuse Reflectance Fourier Transform Infrared Spectrometry," 57(14): 2867 (December 1985).

30. Wallbacks, L., and Edlund, U. etal., *Tappi Journal*, "Multivariate Characterizations of Pulp Using Solid State CNMR, FTIR, and NIR," (10): 201 (1991).

31. Friese, M.A., and Banerjee, S., *Applied Spectroscopy,* "Lignin Determination by FTIR," 46(2): 246 (1992).